

Ultrafast Laser-Induced Phase Transitions in Amorphous GeSb Films

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(Received 15 September 2000)*

Time-resolved measurements of the spectral dielectric function reveal new information about ultrafast phase transitions induced by femtosecond laser pulses in Sb-rich amorphous GeSb films. The excitation generates a nonthermal phase within 200 fs. The dielectric function of this phase differs from that of the crystalline phase, contrary to previous suggestions of a disorder-to-order transition. The observed dielectric function is close to that of the liquid phase, indicating an ultrafast transition from the amorphous phase to a different disordered state.

DOI: 10.1103/PhysRevLett.86.3650

PACS numbers: 78.47.+p, 61.43.Dq, 61.80.Ba, 78.20.Ci

Intense femtosecond laser pulses induce ultrafast, non-thermal phase transitions to disordered, metal-like phases in various materials, starting from both crystalline and amorphous phases [1–6]. In 1998, Sokolowski-Tinten and co-workers presented normal-incidence reflectivity measurements which suggested that femtosecond pulses can induce an ultrafast *disorder-to-order* transition in amorphous GeSb (*a*-GeSb) films [7]. Electron diffraction shows that nano-, pico-, and femtosecond pulses above a certain threshold fluence F_{cr} transform *a*-GeSb permanently to a stable crystalline phase (*c*-GeSb) [8–10]. F_{cr} exceeds the fluence F_m required for melting, and for fluences between F_m and F_{cr} the material reamorphizes on solidification. Sokolowski-Tinten and colleagues found that for *all* fluences above F_{cr} , and *only* those fluences, the normal-incidence reflectivity at 620 nm reaches a value equal to that of the crystalline phase 200 fs after the femtosecond excitation. This suggested a subpicosecond amorphous-to-crystalline phase transition, and raised an important fundamental question: how can lattice ordering occur in less time than it takes to establish thermal equilibrium between the laser-excited electrons and the lattice?

Prompted by this question, we studied *a*-GeSb films following femtosecond excitation by tracking the spectral dielectric function $\epsilon(\omega)$, which reveals the nature of ultrafast phase changes in a material better than the single-frequency reflectivity measurements [4] used in the previous work.

We used a sample identical to that of Ref. [7]: a 50-nm-thick film of amorphous $\text{Ge}_{0.06}\text{Sb}_{0.94}$ deposited on a glass substrate at room temperature in a multitarget dc magnetron sputtering system from pure (99.999%) Ge and Sb targets. We employed a pump-probe technique, in which the sample was excited by a 50-fs, 800-nm pump pulse

from an amplified Ti:sapphire system, and probed by a broadband probe pulse that arrives at a variable time delay after the pump pulse. The 1.5–3.5 eV (820–350 nm) probe pulses were produced by white-light generation [11] from an 800-nm seed pulse in a 2-mm-thick CaF_2 crystal. Different frequencies in the probe pulse arrive at the sample at different times. The results presented below are corrected for the measured temporal dispersion (chirp) of the probe by temporally shifting the data at each frequency. We measured probe reflectivity spectra for *p*-polarized light at two angles of incidence, 52.85° and 79.40°, in order to uniquely determine the real and imaginary parts of $\epsilon(\omega)$ for the GeSb film at each frequency. In numerically inverting the Fresnel reflectivity formulas to obtain $\epsilon(\omega)$, we used a multilayer model [12] to take account of a 1.25-nm-thick SbO_2 oxide layer, for which $\epsilon = 4.2$ [13], and the glass substrate. More details of our experimental technique, including how we determine the oxide thickness, are available elsewhere [14,15].

We confirmed the validity of the technique by measuring the dielectric function of the unexcited *a*-GeSb sample, which matches that measured using ellipsometry with continuous wave white light [13]. To determine the evolution of $\epsilon(\omega)$ after excitation, we measured reflectivity spectra for various time delays between the pump and probe pulses, and for four pump fluences, namely 0.6, 1.2, 1.6, and 4.0 times the threshold for crystallization, which we find to be $F_{cr} = 0.22 \text{ kJ/m}^2$.

Figure 1(a) shows the evolution of the dielectric function following excitation by a pump pulse with $0.6F_{cr}$. Immediately after the excitation, both real and imaginary parts of $\epsilon(\omega)$ shift away from the *a*-GeSb dielectric function, to lower photon energy. This effect can be seen even at zero time delay, when the pump and probe pulses overlap, and the later part of the probe pulse interrogates

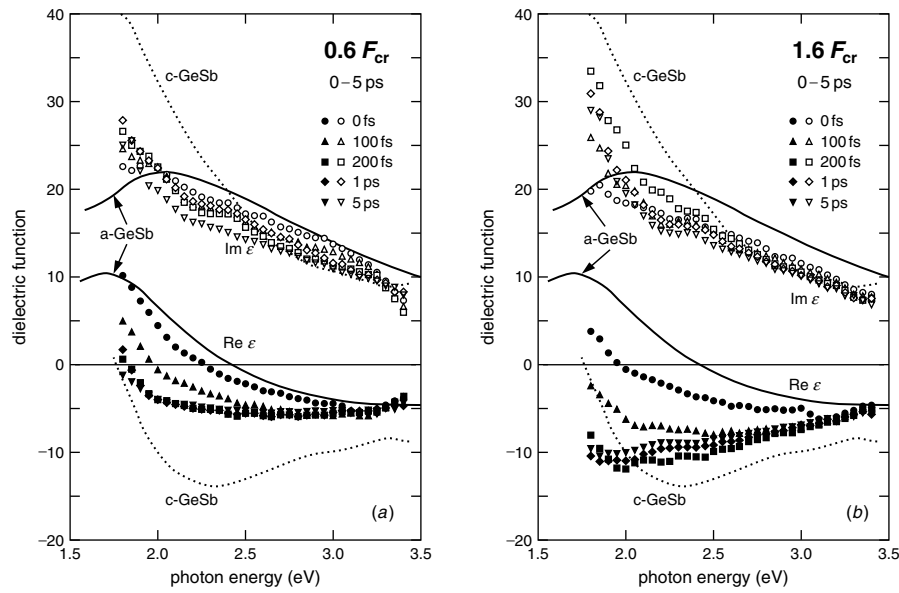


FIG. 1. Evolution of the dielectric function of amorphous $\text{Ge}_{0.06}\text{Sb}_{0.94}$ (filled symbols = $\text{Re}[\epsilon(\omega)]$; open symbols = $\text{Im}[\epsilon(\omega)]$) after excitation by pulses of about (a) 0.6 and (b) 1.6 times the threshold fluence for permanent crystallization. The solid and dotted curves show our measurements of $\epsilon(\omega)$ for unexcited *a*-GeSb and for the *c*-GeSb phase that is permanently induced by pulses above F_{cr} , respectively.

material that the early part of the pump has altered. Over the first 200 fs, the zero crossing of $\text{Re}[\epsilon(\omega)]$ shifts from around 2.4 to 1.8 eV and the peak in $\text{Im}[\epsilon(\omega)]$ moves from 2.1 eV to a frequency beyond the lower edge of our spectral range. From 200 fs until 5 ps, the dielectric function does not change within experimental error. Only after 5 ps does $\epsilon(\omega)$ start to change again (not shown in the figure).

As Fig. 1(b) shows, the dielectric function changes more rapidly, and by a greater amount, for $F = 1.6F_{\text{cr}}$ than for $0.6F_{\text{cr}}$. The data at 200 fs after excitation indicate that the sample is not in the thermodynamically stable crystalline phase: the measured $\epsilon(\omega)$ at 200 fs is clearly different from $\epsilon(\omega)$ for *c*-GeSb. Between 200 fs and 5 ps, the dielectric function changes little ($\text{Re}[\epsilon(\omega)]$ drifts up by about 1 across the spectrum and $\text{Im}[\epsilon(\omega)]$ drifts down by 1–3), and no further alterations occur for delays from 5 ps up to 475 ps (not shown in the figure).

The behavior of the dielectric function at $1.2F_{\text{cr}}$ is identical to that at $1.6F_{\text{cr}}$. At $4.0F_{\text{cr}}$, we observe the same $\epsilon(\omega)$ after 200 fs as at $1.2F_{\text{cr}}$ and $1.6F_{\text{cr}}$. However, at $4.0F_{\text{cr}}$, the material reaches this dielectric function faster—in only 150 fs—and stays at the 200-fs values only until 500 fs to 1 ps after the excitation.

Because the dielectric function after 200 fs is independent of fluence F for $F > F_{\text{cr}}$, we conclude that the material is in a new highly excited phase of the material, in agreement with the previous report [7] based on normal-incidence reflectivity measurements at 2.01 eV. This report suggests that the new phase might be the thermodynamically stable crystalline phase [7], but our dielectric function results reveal that the material transforms to a nonequilibrium phase different from the *c*-GeSb phase.

The new data discard the evidence supporting the notion of a disorder-to-order transition.

The absence of changes in $\epsilon(\omega)$ from 5 to 475 ps at $1.2F_{\text{cr}}$ and $1.6F_{\text{cr}}$ indicates the presence of an optically thick layer during this time period [7,18]. The 5 ps required for this liquid phase to appear is the time it takes for the electrons in GeSb to come into thermal equilibrium with the lattice via electron-phonon coupling and induce thermal melting. This time scale is typical for carrier-lattice equilibration in other materials [4]. Because the dielectric function of liquid $\text{Ge}_{0.06}\text{Sb}_{0.94}$ (*l*-GeSb) is unknown, we shall use one of our measured data sets ($F = 1.6F_{\text{cr}}$, time delay = 100 ps) to represent $\epsilon(\omega)$ for the thermal liquid phase.

Figure 2 compares the normal-incidence reflectivity $R(0^\circ)$ spectra calculated from the measured dielectric function after 200 fs with the corresponding data for amorphous, crystalline, and liquid GeSb. The figure shows that our data are consistent with Ref. [7]: the reflectivity for $F > F_{\text{cr}}$ is the same as that for *c*-GeSb at 2.01 eV. But $R(0^\circ)$ differs at all other photon energies. Furthermore, even at 2.01 eV, we find that for angles of incidence near or above the Brewster angle, the reflectivity does not go to the crystalline level when $F > F_{\text{cr}}$. Thus, our broadband dielectric function measurements demonstrate that the previously reported match in reflectivity values at 2.01 eV is a coincidence. The broadband measurements of $\epsilon(\omega)$ enable one to distinguish phases that may appear the same based on reflectivity or transmission measurements for a single frequency at a single angle of incidence.

What do the dielectric function data indicate about the evolution of GeSb films after excitation, both above and

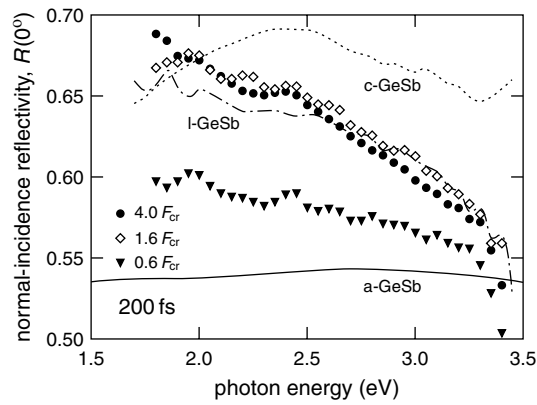


FIG. 2. Reflectivity spectra at normal incidence $R(0^\circ)$ for GeSb at 200 fs after excitation, for different fluences. Also shown are the reflectivity spectra for a -GeSb (solid curves), c -GeSb (dotted curves), and l -GeSb (dash-dotted curves).

below F_{cr} ? Pulses with fluences of order F_{cr} excite about 10^{22} electrons per cm^3 , assuming linear absorption of 800-nm light [10]. Despite generating so many free carriers, there is no evidence of electron-hole plasma effects in our measurements of $\epsilon(\omega)$: during the first 200 fs, the zero crossing of $\text{Re}[\epsilon(\omega)]$ shifts smoothly to lower photon energies. This time scale is longer than the pump pulse duration, which suggests that structural changes are responsible for the observed dynamics of the dielectric function. Such subpicosecond structural changes have been observed in other materials [1–6], and are driven nonthermally by the electronic excitation [16,17].

The dielectric function which appears at 200 fs for $F > F_{cr}$, as a result of the nonthermal structural transition, is well fitted by a Drude model, as shown in Fig. 3. The fit yields a plasma frequency of $\omega_p = 14.5$ eV and relaxation time of $\tau = 0.18$ fs. This plasma frequency implies that almost all the valence electrons are free, i.e., the material is metallic after 200 fs. Although this metallic phase could be a nonequilibrium crystalline phase, it is more likely that the material transforms to a new disordered state. As Fig. 1(b) shows, the dielectric function of this highly excited phase is similar to that observed for time delays of 5 ps and later, when the material is in the liquid phase. Figure 2 reiterates the similarity of the optical properties of the highly excited phase and the liquid phase. This similarity suggests that a -GeSb transforms from the amorphous state, with coordination numbers and packing characteristics close to those of crystalline Sb [18], to a disordered state (either solid or liquid) with coordination numbers and packing characteristics close to those of the liquid. Future time-resolved x-ray diffraction [19] experiments may be able to test this hypothesis because x-ray diffraction is directly sensitive to the lattice structure. In summary, the new evidence suggests that the ultrafast transition is disorder-to-disorder and not disorder-to-order as is currently believed.

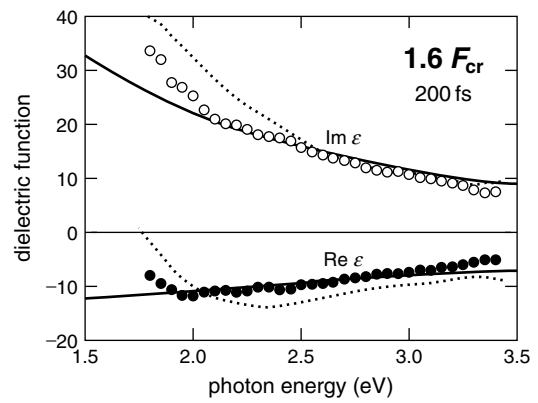


FIG. 3. Drude fit to the dielectric function ($\bullet = \text{Re}[\epsilon(\omega)]$; $\circ = \text{Im}[\epsilon(\omega)]$) of $\text{Ge}_{0.06}\text{Sb}_{0.94}$ at 200 fs after it is excited by a pulse of $1.6F_{cr}$. The solid curve shows the real and imaginary parts of the Drude dielectric function with plasma frequency $\omega_p = 14.5$ eV and relaxation time $\tau = 0.18$ fs. The dotted curve represents $\epsilon(\omega)$ for c -GeSb.

Let us now turn to the results below F_{cr} . Within the first 200 fs after an excitation of $0.6F_{cr}$, the dielectric function changes rapidly, but it remains unchanged for the next 5 ps while the electrons and lattice come into thermal equilibrium. During the first 200 fs, the material may undergo a transition similar to the one observed above F_{cr} but only within an optically thin layer at the surface whose thickness depends on the laser fluence. That is, the probe reflectivity is still affected by the material in the original a -GeSb state that lies below the transformed layer. However, this hypothesis seems unlikely because it would imply that there is no link between the ultrafast phase transition and the permanent crystallization that occurs above F_{cr} , and that it is mere coincidence that the ultrafast transient phase becomes optically thick at the same fluence that causes permanent crystallization. An alternative hypothesis, which is consistent with the experimental data, is the presence of a different nonthermal phase in the first 5 ps at low fluences. Because the reflectivity measured in Ref. [7] at 200 fs below F_{cr} is not independent of fluence, this phase would have to be optically thin.

After 5 ps, once thermal equilibrium is established, the changes in the $0.6F_{cr}$ data can be described by a liquid-layer model, in which the liquid thickness is less than the optical absorption depth and varies with time. We calculate the p reflectivities at 52.85° and 79.40° for five layers: air, 1.25 nm of oxide, x nm of liquid, $(50 - x)$ nm of a -GeSb, and glass substrate. We use the solid-phase value of the dielectric function of the oxide layer, even though it may be molten; our analysis is not qualitatively sensitive to this assumption. Figure 4(a) shows the best fit to the experimental reflectivity spectra at 20 ps after excitation, which yields a value of 12 nm for the sole fitting parameter x . The evolution of x , the liquid-layer thickness, is shown in Fig. 4(b), and indicates that a melt front propagates into the material during the first 20–50 ps. This

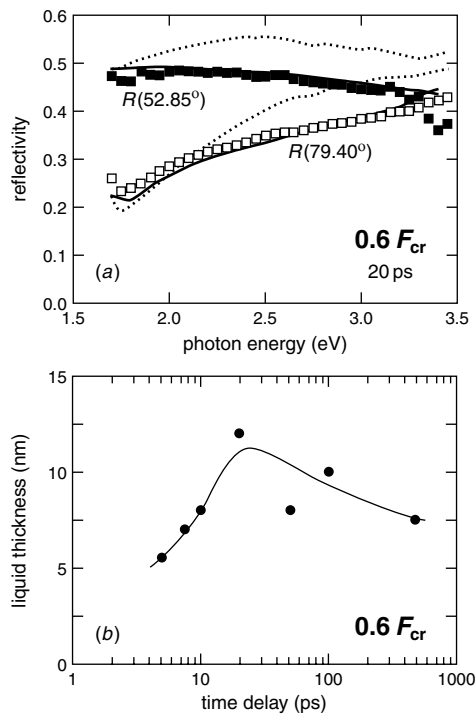


FIG. 4. (a) Liquid-layer model fit (solid curves) with $x = 12$ nm (see text for details) to $R(52.85^\circ)$ and $R(79.40^\circ)$ at 20 ps following excitation with pulses of $0.6 F_{cr}$. The dotted curves show the reflectivities of *c*-GeSb for comparison. (b) Evolution of the liquid-layer thickness. The curve shown is a guide to the eye.

time scale is a reasonable one for heat to diffuse by the absorption depth of the probe light, which is about 10 nm [15]. The maximum in the curve indicates the onset of solidification after about 30–100 ps. This rapid solidification agrees with previous reports of solidification in 25-nm GeSb films on time scales of hundreds of picoseconds following irradiation with 30-ps pulses [20].

In conclusion, we set out to explore the potential for a subpicosecond amorphous-to-crystalline, *disorder-to-order* transition by measuring the dielectric function of *a*-GeSb films following femtosecond laser excitation. We observe subpicosecond nonthermal structural changes both above and below the threshold for permanent crystallization F_{cr} . The results confirm that there is a phase transition within 150–200 fs for $F > F_{cr}$, i.e., one whose occurrence is correlated with the observation of a

permanent amorphous-to-crystalline transition. However, the ultrafast transition does not lead to the thermodynamically stable crystalline phase, but to a nonequilibrium disordered phase—and is therefore a *disorder-to-disorder* transition.

We thank C. Arnold, A. Brodeur, E. Kaxiras, and K. Sokolowski-Tinten for many valuable discussions. The work at Harvard is supported by the National Science Foundation (Contract No. DMR-9807144) and the Army Research Office (Contract No. DAAG55-98-1-0077). A.M.-T. Kim recognizes support from the Deutscher Akademischer Auslandsdienst (DAAD) and J. Siegel from the European Union through the TMR Program (Grant No. ERB40001GT954352).

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